

# PATENT COOPERATION TREATY

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From the  
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

Rec'd PCT/PTO 31 JAN 2005  
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## NOTIFICATION OF TRANSMITTAL OF THE INTERNATIONAL PRELIMINARY EXAMINATION REPORT (PCT Rule 71.1)

Date of mailing (day/month/year) 18.10.2004			
Applicant's or agent's file reference 3484PTWO/er	<b>IMPORTANT NOTIFICATION</b>		
International application No. PCT/EP 03/08350	<table border="1"> <tr> <td>International filing date (day/month/year) 29.07.2003</td> <td>Priority date (day/month/year) 01.08.2002</td> </tr> </table>	International filing date (day/month/year) 29.07.2003	Priority date (day/month/year) 01.08.2002
International filing date (day/month/year) 29.07.2003	Priority date (day/month/year) 01.08.2002		
Applicant UNIVERSITA' DEGLI STUDI DI TRIESTE et al.			

1. The applicant is hereby notified that this International Preliminary Examining Authority transmits herewith the international preliminary examination report and its annexes, if any, established on the international application.
2. A copy of the report and its annexes, if any, is being transmitted to the International Bureau for communication to all the elected Offices.
3. Where required by any of the elected Offices, the International Bureau will prepare an English translation of the report (but not of any annexes) and will transmit such translation to those Offices.
4. **REMINDER**

The applicant must enter the national phase before each elected Office by performing certain acts (filing translations and paying national fees) within 30 months from the priority date (or later in some Offices) (Article 39(1)) (see also the reminder sent by the International Bureau with Form PCT/IB/301).

Where a translation of the international application must be furnished to an elected Office, that translation must contain a translation of any annexes to the international preliminary examination report. It is the applicant's responsibility to prepare and furnish such translation directly to each elected Office concerned.

For further details on the applicable time limits and requirements of the elected Offices, see Volume II of the PCT Applicant's Guide.

The applicant's attention is drawn to Article 33(5), which provides that the criteria of novelty, inventive step and industrial applicability described in Article 33(2) to (4) merely serve the purposes of international preliminary examination and that "any Contracting State may apply additional or different criteria for the purposes of deciding whether, in that State, the claimed inventions is patentable or not" (see also Article 27(5)). Such additional criteria may relate, for example, to exemptions from patentability, requirements for enabling disclosure, clarity and support for the claims.

Name and mailing address of the international preliminary examining authority:



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**PATENT COOPERATION TREATY**  
**PCT**  
**INTERNATIONAL PRELIMINARY EXAMINATION REPORT**  
(PCT Article 36 and Rule 70)

Applicant's or agent's file reference 3484PTWO/er	<b>FOR FURTHER ACTION</b> See Notification of Transmittal of International Preliminary Examination Report (Form PCT/PEA416)	
International application No. PCT/EP 03/08350	International filing date ( <i>day/month/year</i> ) 29.07.2003	Priority date ( <i>day/month/year</i> ) 01.08.2002
International Patent Classification (IPC) or both national classification and IPC C01B31/02		
Applicant UNIVERSITA' DEGLI STUDI DI TRIESTE et al.		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.
2. This REPORT consists of a total of 5 sheets, including this cover sheet.
- ☒ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).
- These annexes consist of a total of 10 sheets.

3. This report contains indications relating to the following items:

- I ☒ Basis of the opinion
- II ☐ Priority
- III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- IV ☐ Lack of unity of invention
- V ☒ Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI ☐ Certain documents cited
- VII ☐ Certain defects in the international application
- VIII ☐ Certain observations on the international application

Date of submission of the demand  27.02.2004	Date of completion of this report  18.10.2004
Name and mailing address of the international preliminary examining authority:  European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized Officer  Marucci, A  Telephone No. +49 89 2399-7819 

**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT**

International application No. **PCT/EP 03/08350**

**I. Basis of the report**

1. With regard to the **elements** of the international application (*Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17))*):

**Description, Pages**

1 as originally filed  
2-8 received on 29.06.2004 with letter of 23.06.2004

**Claims, Numbers**

1-10 received on 29.06.2004 with letter of 23.06.2004

**Drawings, Sheets**

1/2-2/2 as originally filed

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).  
☐ the language of publication of the international application (under Rule 48.3(b)).  
☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in written form.  
☐ filed together with the international application in computer readable form.  
☐ furnished subsequently to this Authority in written form.  
☐ furnished subsequently to this Authority in computer readable form.  
☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.  
☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- ☐ the description, pages:  
☐ the claims, Nos.:  
☐ the drawings, sheets:

**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT**

International application No. **PCT/EP 03/08350**

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)).

*(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)*

6. Additional observations, if necessary:

**V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement**

1. Statement

Novelty (N)	Yes: Claims	1-10
	No: Claims	
Inventive step (IS)	Yes: Claims	1-8
	No: Claims	9-10
Industrial applicability (IA)	Yes: Claims	1-10
	No: Claims	

2. Citations and explanations

**see separate sheet**

**Re Item V**

**Reasoned statement with regard to novelty, inventive step or industrial applicability;  
citations and explanations supporting such statement**

1- Reference is made to the following document:

D1: GEORGAKILAS V. ET AL: "Organic Functionalization of Carbon Nanotubes" J. AM. CHEM. SOC., vol. 124, no. 5, 6 February 2002 (2002-02-06), pages 760-761, XP002262088

**2- Positive statement regarding claims 1-8:**

The document D1 is regarded as being the closest prior art to the subject-matter of claim 1, and shows (the references in parentheses applying to this document):  
a method for functionalizing and dissolving carbon nanotubes through a 1,3-dipolar cycloaddition of azomethine ylides, generated by condensation of an  $\alpha$ - amino acid and an aldehyde (page 1, column 1, 4<sup>th</sup> and 5<sup>th</sup> paragraphs; Scheme 1).

The subject-matter of claim 1 differs from this known article in that the functionalized carbon nanotubes are purified from their carbon and metal contaminants by an additional treatment (novelty in the sense of Art. 33(2) PCT).

No hint could be found in document D1 which would suggest the possibility of using the process therein disclosed to purify carbon nanotubes. The subject-matter of claim 1 involves, therefore, an inventive step in the sense of Art. 33(3) PCT.

Claims 2-8 are dependent on claim 1 and as such also meet the requirements of the PCT with respect to novelty and inventive step.

**3- Negative statements regarding claims 9 and 10:**

**3.1- Claim 9** discloses functionalized carbon nanotubes obtainable by a 1,3-dipolar reaction with an aldehyde and an amino-acid. Even though the reactants used in document D1 for performing the same kind of reaction are part of those excluded in claim 9, an inventive step cannot be accorded as the compounds disclosed in claim 9 and in D1 are structurally very close. To accord an inventive step, the novel compounds in claim 9 should

exhibit a use or an effect which is unexpected with respect to the teaching of D1, which is not the case of this application.

Therefore, the subject-matter of claim 9 does not involve an inventive step (**Art. 33(3) PCT**).

**3.2-** Dependent **claim 10** does not contain any features which, in combination with the features of any claim to which it refers, meet the requirements of the PCT in respect of inventive step, see document D1 and the corresponding passages cited in the search report.

**3.3-** Claim 9 does not meet the requirements of **Article 6 PCT** in that the matter for which protection is sought is not clearly defined. The claim attempts to define a product in terms of process features. It appears, however, possible to define the subject-matter in more concrete terms, viz. in terms of the characteristics of the products obtainable through the process to which the claim refers. The claim should, therefore, be appropriately reformulated.

purification, the first problem to be overcome is the question of their insolubility. For this aspect the initial material, before actual purification, is subjected in many cases to drastic dispersion processes in solvents or in water, such as pulverization, sonication or ultrasonication with or without surfactants. In any case these are purification processes that require several phases, even at high temperatures, in which the oxidizing treatment(s) with acids are essential and preferred to eliminate both metal and carbon contaminants. However, in this way the nanotubes are also impaired, destroying a part of them and introducing numerous structural defects with considerable influences on their chemico-physical and mechanical properties.

Chiang I.W. et al. (J. Phys. Chem. B 2001, 105, 8297-8301) describes a SWNT purification method through a high temperature oxidization process, obtaining a yield of about 30% and a high degree of purity. Nonetheless, this purification method, in addition to obtaining low yield rates, has the disadvantage of also oxidizing the NT, with consequent modifications in their molecular structure.

Therefore, as it is currently impossible to purify the nanotubes with a high degree of yield and purity at industrial level in a manner that safeguards them, they are usually marketed as they are produced.

In view of the fact that however they are fabricated, nanotubes are extremely costly materials and that for some industrial uses unshortened nanotubes without structural defects are preferred, the object of the present invention is to establish a purification method industrially applicable to the raw material, which has a good yield rate both as regards quantity and quality and which does not impair the structure of the nanotubes.

#### **Summary of the invention**

A new, non-destructive purification process for industrially produced carbon nanotubes (pristine nanotubes p-NT), both SWNT and MWNT, has now been found, and is the object of the present invention, characterized by at least the following steps:

- solubilization of the carbon nanotubes (p-NT) through their organic functionalization in which the functionalization reaction is obtained on the

AMENDED SHEET

carbon nanotubes with 1,3-dipolar reaction of azomethine ylides and separation from metal contaminants,

- purification from carbon contaminants of functionalized carbon nanotubes (f-NT) obtained in the previous step by precipitation with solvents from their organic solutions,
- heat treatment of functionalized carbon nanotubes obtained in the previous step to regenerate the initial non-functionalized carbon nanotubes free of metal and carbon contaminants.

A further object of the invention relates to new functionalized carbon nanotube obtained with the 1,3-dipolar reaction of functionalization azomethine ylides according to the first step.

#### **Brief description of the drawings**

FIGURE 1: Transmission electron microscopy (TEM) images of pristine single – walled carbon nanotube (p-SWNT);

FIGURE 2: Transmission electron microscopy (TEM) image of functionalized single – walled carbon nanotube (f-SWNT);

FIGURE 3: Transmission electron microscopy (TEM) images of de-functionalized single - walled carbon nanotube at the end of purification process.

#### **Detailed description of the invention**

Solubilization of carbon nanotubes, both SWNT and MWNT, through functionalization has been described by inventors starting out with materials prepared and purified according to conventional procedures (Georgakilas G. et. al. J. Am. Chem. Soc. 2002, 124, 760-761).

To attain the object of the present invention, the purification process involved in the present invention is characterized by the following phases:

- solubilization through organic functionalization of carbon nanotubes as produced industrially (pristine nanotubes p-NT) through 1,3-dipolar reaction of azomethine ylides and separation from metal contaminants,
- purification of functionalized carbon nanotubes (f-NT) by precipitation with solvents from organic solutions of functionalized nanotubes,
- heat treatment of functionalized carbon nanotubes (f-NT) to regenerate the initial non-functionalized nanotubes.



When establishing the purification process described it was unexpectedly discovered that the functionalization reaction of the carbon nanotubes can also be obtained when the initial material is a raw material containing metal contaminants deriving from industrial production and that each of the phases required

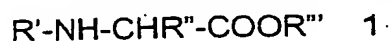
5 contributes towards purification of the initial raw product, but that only through a combination of these is a final product with a high level of purity obtained.

In detail, the purification method established is as described hereunder.

The industrial carbon nanotubes (p-NT), represented by raw material produced according to any one of the production processes mentioned hereinbefore, are

10 functionalized through a 1,3-dipolar reaction which involves the p-nanotubes and the following components:

a) compounds with a general formula 1



where R', R'' and R''' equal to or different from one another may be:

15 H or alkyl groups with the formula  $C_nH_{2n+1}$  with n between 1 and 20, or an aromatic group, or limited to R', R''' an ether group with the formula  $(CH_2CH_2O)_n$  with n between 1 and 20 and

b) compounds with a general formula 2



20 where R'''' may be H or an alkyl group with the formula  $C_nH_{2n+1}$  with n between 1 and 20, or an ether group with the formula  $(CH_2CH_2O)_n$  with n between 1 and 20, or an aromatic group.

The functionalization reaction is conducted in a dipolar aprotic solvent chosen from the group constituted by dimethylformamide (DMF), dimethylsulphoxide, sulpholane, orthodichlorobenzene with reagents in excess and temperature over

25 100°C for at least 24 hours.

Any functionalized carbon nanotubes obtained through the 1.3-dipolar reaction of azomethine ylides, being soluble, can be used in the purification process of p-nanotubes. Furthermore, respect to the paper cited (Georgakilas G. et. al., 2002, ref.cit.), the functionalized carbon nanotubes obtained through the reaction above

30 mentioned are also new except when R', R'', R''' and R'''' are equal to one another and equal to H; R' is equal to an ether group with the formula -

(CH<sub>2</sub>CH<sub>2</sub>O)<sub>3</sub>-CH<sub>3</sub> and R'', R''' and R'''' are equal to one another and equal to H; R' is equal to an alkyl group with the formula -CH<sub>2</sub>(CH<sub>2</sub>)<sub>6</sub>CH<sub>3</sub> and R'', R''' and R'''' are equal to one another and equal to H; R' is equal to an ether group with the formula -(CH<sub>2</sub>CH<sub>2</sub>O)<sub>3</sub>-CH<sub>3</sub>, R'', R''' are equal to each other and equal to H and R'''' is equal to -phenyl-OCH<sub>3</sub>; R' is equal to an ether group with the formula - (CH<sub>2</sub>CH<sub>2</sub>O)<sub>3</sub>-CH<sub>3</sub>, R'', R''' are equal to each other and equal to H and R'''' is equal to a pyrene group.

Purely for non-limiting explanatory purposes of the present invention, a typical process for functionalization of commercial carbon nanotubes is described hereunder.

Example 1: organic functionalization reaction

100 mg of SWNT carbon nanotubes are suspended in 300 ml of dimethylformamide (DMF). The mixture is heated to 140°C and a solution of N-octylglycine ethyl ester in DMF (500 mg in 10 ml) is added in portions of 2 ml every 24 hours with 500 mg of paraformaldehyde each time. Lastly, after 50 hours, 500 mg of N-octylglycine ethyl ester and 2.5 g of aldehyde are added to the initial suspension. The mixture is heated for a further 72 hours.

Example 2: organic functionalization reaction

100 mg of SWNT carbon nanotubes are suspended in 300 ml of dimethylformamide (DMF). The mixture is heated to 140°C and a solution of N-methylglycine in DMF (500 mg in 10 ml) is added in portions of 2 ml every 24 hours with 500 mg of n-heptaldehyde each time. Lastly, after 50 hours, 500 mg of N-methylglycine and 2.5 g of aldehyde are added to the initial suspension. The mixture is heated for a further 72 hours.

In both examples the organic phase is separated by filtration on paper under vacuum and the solution is transferred to a rotary evaporator where the DMF is removed quantitatively. The remaining brown oily residue is diluted in 200 ml of dichloromethane and washed with water (5x200 ml). The organic phase is dried over Na<sub>2</sub>SO<sub>4</sub> and after being filtered (to remove the Na<sub>2</sub>SO<sub>4</sub>) the solution is concentrated under vacuum. The residue is dissolved in 2 ml of dichloromethane and subsequently 10 ml of methanol is added to the mixture. The solid part that

surfaces after adding the methanol is separated by centrifugation or filtering and washed repeatedly with methanol, until the alcohol phase no longer colours.

The products resulting from this reaction (functionalized carbon nanotubes f-NT) have a high level of solubility in organic solvents, in which the metal particles present remain insoluble and are therefore eliminated with conventional mechanical means such as filtration under vacuum, centrifugation, etc.. The organic phase containing the f-NT is concentrated to eliminate the reaction solvent and the residue is dissolved in polar or apolar solvents chosen from the group constituted by dichloromethane, chloroform, toluene, washed several times with water. The organic phase is then dried and concentrated after removing the drying agent.

The functionalized carbon nanotubes (f-NT) again solubilized in polar or apolar solvents chosen from the group constituted by dichloromethane, chloroform, toluene are then precipitated with one or more treatments with polar or apolar solvents chosen from the group constituted by diethylether, petroleum ether, alkanes, alcohols, separated with mechanical means (for example centrifugation or filtration) and washed once or several times with the same solvent used for precipitation.

The precipitated carbon nanotubes (f-NT) obtained are again dissolved with organic solvents chosen from the group constituted by chloroform and methylene chloride. The subsequent precipitation phase, as described hereinbefore, is performed with polar or apolar organic solvents chosen from the group constituted by diethylether, petroleum ether, alkanes, alcohols, separated with mechanical means (for example centrifugation or filtration). In this phase the contaminants constituted by amorphous carbon materials remaining in solution are eliminated and therefore precipitations with solvents may be one or several according to the degree of purity to be obtained. The precipitation phase can be repeated several times on the carbon nanotubes remaining in the solution until no precipitates are obtained.

The purified f-NT deriving from the precipitation phase are then defunctionalized by dry heating in an atmosphere with air, or inert gases, such as nitrogen or argon, or preferably under vacuum, at temperatures ranging from 250° to 350°C for times

between 1 minute and one hour. The initial carbon nanotubes, without the contaminants from industrial production, are thus obtained after heat treatment with mechanical means chosen from centrifugation and filtration of suspensions obtained by sonication of these in polar or apolar solvents chosen from the group constituted by dichloromethane, chloroform, toluene.

Purely for non-limiting explanatory purposes of the present invention, a typical purification process performed on functionalized carbon nanotubes is described hereunder.

Example 3: purification of functionalized carbon nanotubes

80 mg of functionalized carbon nanotubes according to example 1 and obtained using N-(CH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>)-glycine with paraformaldehyde are dissolved in 300 ml of CHCl<sub>3</sub>. In this way a transparent brown solution is obtained. Diethylether is added in drops to the solution under stirring at ambient temperature. This is added until a precipitate appears. The solution is filtered and diethylether is once again added. The precipitate is recovered from the paper filter dissolving it in CH<sub>2</sub>Cl<sub>2</sub>. After the CH<sub>2</sub>Cl<sub>2</sub> has evaporated, the solid material is washed with diethylether, centrifuged and dried under vacuum. This procedure is repeated three times; three precipitates (P1, P2 e P3) are obtained. Moreover, after evaporation of the chloroform, the material that had not yet precipitated (S) is also obtained in solid state.

The precipitates P1, P2 and P3 appear respectively after the addition of 480, 300 and 300 ml of diethylether, each of these precipitates is equal to about 10 mg; S is equal to 50 mg with a total yield of 100%.

The purity of each of these fractions is determined by TEM analysis.

Example 4: defunctionalization and regeneration of carbon nanotubes.

2 mg of functionalized carbon nanotubes are placed in a metal (aluminium) capsule and heated to 300°C under a flow of nitrogen for 30 minutes. The capsule is transferred to a conical flask containing 20 ml of dichloromethane, where the content of the capsule is freed in suspension in the organic phase through 10-20 sec of sonication in a normal ultrasonic bath. The solid product is separated by centrifugation or filtering, washed with 10 ml of chloroform and dried under vacuum for 2 hours. At the end of this step 1.4 mg of purified carbon nanotubes

have been obtained with a yield of 100%.

The results obtained with the process described are set down hereunder.

Fig.1 shows transmission electron microscopy (TEM) of the carbon nanotubes (p-SWNT) before functionalization and precipitation containing high quantities of metal

particles and carbon materials and fig. 2 those obtained after functionalization (f-SWNT) with no traces of metal particles and with no carbon materials.

Fig. 3 shows the TEM photographs obtained on the carbon nanotubes after precipitation with solvents and heat treatment.

Moreover, it must be pointed out that the initial carbon nanotubes (p-SWNT) and those obtained at the end of the purification process after heat treatment (r-SWNT) were subjected to UV-Vis-NIR and IR-Raman analysis. The results show that the two types of carbon nanotubes have the same electronic behaviour, confirming that the purification process has not caused any structural damage to the carbon nanotubes thus purified.

Substantially, by adopting the purification process described, the same results are obtained starting out with p-SWNT and with the p-MWNT type. Without departing from the scope of the invention it is possible for those skilled in the art to make all the modifications and improvements to the process described in and the object of the present invention suggested by normal experience and development in the technique.

## CLAIMS

1. Purification process of carbon nanotubes characterized in that it comprises at least the following steps.

- solubilization of the carbon nanotubes (p-NT) through their organic functionalization in which the functionalization reaction is obtained on the nanotubes with 1,3-dipolar reaction of azomethine ylides and separation from metal contaminants,
- purification from carbon contaminants of functionalized carbon nanotubes (f-NT) obtained in the previous step by precipitation of functionalized carbon nanotubes with solvents from their organic solutions,
- heat treatment of functionalized carbon nanotubes obtained in the previous step to regenerate the initial non-functionalized carbon nanotubes free from traces of metal and carbon contaminants.

2. Purification process of carbon nanotubes as claimed in claim 1 wherein the carbon nanotubes are functionalized through a 1,3-dipolar reaction with:

a) compounds with a general formula 1



where R', R'' and R''' equal to or different from one another may be H or alkyl groups with the formula  $C_nH_{2n+1}$  with n between 1 and 20, or an aromatic group, or limited to R', R''' an ether group with the formula  $(CH_2CH_2O)_n$  with n between 1 and 20 and

b) compounds with a general formula 2



where R''' may be H or an alkyl group with the formula  $C_nH_{2n+1}$  with n between 1 and 20, or an ether group with the formula  $(CH_2CH_2O)_n$  with n between 1 and 20, or an aromatic group.

3. Purification process of carbon nanotubes as claimed in claim 2 wherein the 1,3-dipolar reaction is conducted in dipolar aprotic solvent chosen from the group constituted by dimethylformamide (DMF), dimethylsulphoxide, sulpholane, orthodichlorobenzene with reagents in excess and temperature over 100°C for at least 24 hours.

4. Purification process of carbon nanotubes as claimed in claim 1 wherein the separation from metal contaminants is obtained with mechanical means chosen from filtration and centrifugation of the organic solution deriving from the functionalization reaction of raw carbon nanotubes.

5. Purification process of carbon nanotubes as claimed in claim 1 wherein purification from carbon contaminants is obtained starting out with an organic solution containing functionalized carbon nanotubes in polar or apolar solvents, chosen from the group constituted by methylene chloride and chloroform, by precipitation with one or more treatments with polar or apolar solvents, chosen from the group constituted by diethylether, petroleum ether, alkanes, alcohols and separation with mechanical means chosen from centrifugation and filtration.

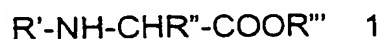
6. Purification process of carbon nanotubes as claimed in claim 1 wherein the initial carbon nanotubes are obtained by dry heating the functionalized carbon nanotubes in an atmosphere with air or inert gases at temperatures ranging from 250° to 350°C for times between 1 minute and one hour.

7. Purification process of carbon nanotubes as claimed in claim 1 wherein the initial carbon nanotubes are obtained by dry heating the functionalized carbon nanotubes at temperatures ranging from 250° to 350°C for times between 1 minute and one hour under vacuum.

8. Purification process of carbon nanotubes as claimed in claim 6 and 7 wherein the initial carbon nanotubes defunctionalized by heat treatment are separated with mechanical means chosen from centrifugation and filtration of their suspensions obtained by sonication in polar or apolar organic solvents chosen from the group constituted by dichloromethane, chloroform, toluene.

9. Functionalized carbon nanotubes obtained with 1,3-dipolar reaction with the carbon nanotubes and:

a) compounds with a general formula 1



where R', R'' and R''' equal to or different from one another may be H or alkyl groups with the formula  $C_nH_{2n+1}$  with n between 1 and 20, or an aromatic group, or

limited to R', R'' an ether group with the formula  $(\text{CH}_2\text{CH}_2\text{O})_n$  with n between 1 and 20 and

b) compounds with a general formula 2



5 where R''' may be H or an alkyl group with the formula  $\text{C}_n\text{H}_{2n+1}$  with n between 1 and 20, or an ether group with the formula  $(\text{CH}_2\text{CH}_2\text{O})_n$  with n between 1 and 20, or an aromatic group

except for compounds in which: R', R'', R''' and R'''' are equal to one another and equal to H; R' is equal to an ether group with the formula  $-(\text{CH}_2\text{CH}_2\text{O})_3\text{-CH}_3$  and  
 10 R'', R''' and R'''' are equal to one another and equal to H; R' is equal to an alkyl group with the formula  $-\text{CH}_2(\text{CH}_2)_6\text{CH}_3$  and R'', R''' and R'''' are equal to one another and equal to H; R' is equal to an ether group with the formula  $-(\text{CH}_2\text{CH}_2\text{O})_3\text{-CH}_3$ , R'', R''' are equal to each other and equal to H and R'''' is equal to  $-\text{phenyl-OCH}_3$ ; R' is equal to an ether group with the formula  
 15  $(\text{CH}_2\text{CH}_2\text{O})_3\text{-CH}_3$ , R'', R''' are equal to each other and equal to H and R'''' is equal to a pyrene group.

10. Functionalized carbon nanotubes obtained with 1,3-dipolar reaction as claimed 9 in which said reaction is conducted in a dipolar aprotic solvent chosen from the group constituted by dimethylformamide (DMF), dimethylsulphoxide,  
 20 sulpholane, orthodichlorobenzene with reagents in excess and temperature over  $100^\circ\text{C}$  for at least 24 hours.